Summary
(Infiltration and Distribution of Ethanol and Ethanol-blended Gasoline in the Vadose Zone)

We have very little information on the behavior of ethanol-containing gasoline as it infiltrates through the unsaturated zone. To better understand these unsaturated zone processes, additional research was conducted. The research presented in this chapter found that the addition of ethanol to gasoline changes the nature of the capillary phenomena affecting gasoline infiltration and distribution at the water table due to the extensive and rapid partitioning of ethanol in to soil moisture and the associated reduction in the interfacial and surface tension between the phases. These changes affect the environmental behavior of gasoline containing ethanol in the following ways:

- There is less residual gasoline entrapped in the unsaturated zone following the spill of ethanol-blended gasoline compared with a standard gasoline. The reduced surface and interfacial tension in the presence of ethanol ultimately results in more complete drainage of fluids from the region.
- A significant fraction of ethanol partitions into, and is retained by, the residual water in the unsaturated zone during gasoline infiltration. Depending on the volume of the spill, this ethanol could then drain slowly into the gasoline pool, creating a central region with high ethanol concentration. The remainder of the pool appears much the same as a spill of gasoline without ethanol.
- The fraction of ethanol retained in the unsaturated zone depends greatly on the volume of soil involved, the water content, and the rate that gasoline enters the subsurface. The rate that the ethanol-laden water in the unsaturated zone drains to the capillary fringe is limited by the increased viscosity and, therefore, reduced unsaturated hydraulic conductivity of this phase. Functional relationships to describe these processes have not yet been developed.

Bulk ethanol releases at distribution terminals can affect the behavior of previously released fuel hydrocarbons in the following ways:

- Bulk ethanol dissolves and mobilizes light nonaqueous phase liquid (LNAPL) entrapped in the unsaturated and saturated zones. This process creates regions in the vadose zone with high saturation that can drain towards the capillary fringe. The net result is a substantial decrease in the LNAPL entrapped in the unsaturated zone.
- Ethanol creates a capillary fringe depression into which all nearby LNAPL can drain. The reduction in surface tension, and, therefore, the height of the capillary fringe in the region that ethanol infiltrates, essentially creates a depression into which all nearby LNAPL can drain. The LNAPL in this region has a reduced interfacial tension, allowing it to fill a greater fraction of the pore spaces. The net result is a region with high LNAPL saturation that would be very mobile.

- The wetting properties of soils could change as the result of a bulk ethanol spill. At a bulk ethanol release site with fuel hydrocarbons present, it appears that significant surfactant concentrations, which affect capillary properties, exist in the aqueous phase. It is possible that their presence could be related to the stimulation of the microbial community in the presence of ethanol. Additional research would be required to confirm these mechanisms.

The results of research presented in this chapter suggest that there is still significant uncertainty in the magnitude of the effects examined. For a ethanol-blended gasoline spill, uncertainty in the amount of ethanol that is retained in the unsaturated zone prevents us from adequately predicting the composition of gasoline that accumulates in a pool at the capillary fringe and, therefore, the flux of contaminants from the source area into groundwater. Additional research is needed at several levels to provide sufficient information to predict ethanol and BTEX fluxes to groundwater. The specific vadose zone studies that are recommended include:

- Laboratory studies to better quantify the functional relationships that control the retention of ethanol in the unsaturated zone. These studies should examine the retention of ethanol as a function of soil type, moisture content and spill rate, and should include laboratory tests to better define the significance of the observed reversal from water wetting to LNAPL wetting.
- Numerical modeling. Improved modeling efforts are needed to better represent the complex behavior of gasoline LNAPL in the presence of ethanol. A spill of ethanol-blended gasoline into the subsurface should not be modeled as a pool of gasoline with constant composition throughout. This modeling should include the partitioning of ethanol into the aqueous phase of the unsaturated zone as well as the resulting change in interfacial properties, flow characteristics, and cosolvency.
- A field-scale test that includes the release of ethanol blended gasoline under unsaturated conditions. A field-scale controlled release is needed to validate in the field processes observed in the laboratory and to calibrate predictive models of the long-term net flux of ethanol and BTEX into groundwater.

Although mostly qualitative, the results of this investigation also provide a basis for recommendations regarding the remediation of soil contaminated with ethanol or ethanol-blended gasoline:

- Increased mobility can enhance LNAPL recovery. Because the spill of ethanol into soil previously contaminated by an LNAPL consolidates the LNAPL into a pool with high mobility, an opportunity exists for effective free-phase recovery of the LNAPL that would have not have otherwise been available. Efforts to recover this LNAPL should be made in a timely fashion.
- Enhanced bioremediation within the unsaturated zone. The retention of ethanol in the unsaturated zone after the spill of ethanol-blended gasoline could provide an opportunity for biodegradation of the ethanol prior to its entry into the saturated groundwater zone. Oxygen, which is likely to become limited, should be added to the unsaturated zone in some form to enhance the rate of ethanol degradation in this region.